ALCOHOL AIR FUEL CELLS - DEVELOPMENT AND APPLICATION

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INTRODUCTION

Taitelbaum (1) in 1910 was the first to convert the chemical energy of liquid fuels (e.g. petroleum, stearic acid and starch) in a galvanic cell into electricity. But the use of fuels like alcohols or aldehydes was proposed many years later by Kordesch and Marko (2) and by Justi et al (3).

Kordesch and Marko studied the system formaldehyde/air. The cell with the alkaline or acid electrolyte contains an oxygen diffusion electrode and a porous fuel electrode. The fuel or fuel/electrolyte mixture penetrates the fuel electrode from the back. In this manner an enlargement of the two phase boundary is obtained. Moreover, under proper operating conditions the fuel concentration is relatively small in the vicinity of the oxygen electrode, even if no diaphragm is used. This is particularly important if the oxygen electrode contains a metal which catalyses the fuel reaction.

In an other method of construction the alcohol is dissolved in the electrolyte and both electrodes dip into the fuel-electrolyte mixture (3,4).

The use of liquid fuels in general obviates the need for a three-phase boundary, and thus facilitates the construction of the fuel electrode. An additional advantage is that the fuel can be brought to the catalytic electrode in high concentration. Thus, if the reaction is fast enough, high current densities can be obtained (up to 1 A/cm^2 at room temperature). Such battery systems can be used conveniently for maintenance-free, continuous operation if air at ambient temperature and pressure is supplied to the oxygen electrode. Some examples of this type of fuel cell are discussed in the following.

METHANOL AIR CELL FOR OPERATION AT LOW CURRENT DENSITIES

General Remarks

In recent experiments (5,6) it has been shown, that the anodic oxidation of methanol proceeds via formaldehyde, and formate or formic acid respectivly. On open circuit at platinum metal electrodes one observes a hydrogenation/dehydrogenation-equilibrium (7), while under load also methanol is not electrochemically active itself. At potentials $\varphi <$ + 400 mV versus the H_2 potential in the same solution a preliminary dehydrogenation takes place. At more positive potentials the fuel reacts with the oxygen which has been chemically adsorbed by the electrode surface (8,9). Therefore, a suitable combination of catalyst, electrolyte and temperature has to be arranged to obtain the required current density in the desired potential range over the total oxidation up to CO_2 or CO_3^{--} respectively. In this connection two problems have to be solved when using an alkaline solution, which is the most suitable electrolyte for practical cells.

(i) An appreciable enrichment of formate has to be avoided: the use of mixed platinum and palladium catalysts is one possible solution (10).

(ii) The electrode polarization increases with the concentration of CO_3^{--}-ions at current densities $j > 5 - 10$ mA/cm^2 at 20 - 50°C (11). To obtain a flat voltage/time curve over the total capacity of 6 electrons per molecule (i.e. $CH_3OH + 8\ OH^- \longrightarrow CO_3^{--} + 6\ H_2O + 6\ e^-$), the critical current density should not therefore be exceeded.

Experimental Results with Laboratory Cells

For the investigation in the laboratory glass vessels containing 1 liter of electrolyte/fuel mixture (10 N KOH and 4.5 M methanol) were used. KOH is used because cells with NaOH have higher polarizations, particularly on the oxygen side. The KOH concentration is chosen in such a manner that even after complete reaction of the fuel the OH^--concentration will be 1 - 2 molar.

Platinum on a porous carrier was found to be a better catalyst than Raney-nickel. Up to now 2 - 5 mg Pt/cm^2 have been used. At this fuel electrode the oxidation potentials for methanol and formate up to current densities of 5 mA/cm^2 are about the same. So the formate content of the electrolyte when using methanol as fuel is very low. This results in a flat voltage-time curve (see Fig. 1).

Since, for the intended application (see below), only a few mA/cm^2 are needed, porous carbon without metallic additions is used on the oxygen side. Plate-like or cylindrical electrochemically active carbon electrodes (surface area: 250 cm^2) are made hydrophobic with polyethylene dissolved in benzene to such a degree that the methanol/electrolyte mixture will not penetrate through the electrode even after 10.000 hours (the thickness of the electrode plates is 5 - 10 mm).

The EMF of this methanol/air cell is about 0.9 volt; at a current drain of 0.5 amp the terminal voltage is 0.75 - 0.6 volt. For short periods of time 2 amps can be withdrawn at 0.6 - 0.5 volt. The long term experiments are performed taking into consideration that the end use will be periodic loads (2 seconds at 0.5 amp and 4 seconds O.C.). The periodic current interruption not only makes the diffusion of air easier but it also increases the life time and preserves the activity of the fuel electrode.

Typical discharge curves are shown in Fig. 1. The difference between theoretical and experimental current yields can be explained on the basis of analysis of the electrolyte by evaporation of methanol through the porous carbon. The analysis also shows that the diffusion of CO_2 from the air through the carbon can be neglected.

The influence of temperature on the oxidation rate at constant electrode potential is very pronounced. Current density-potential plots obtained after operation for one day at 10 mA/cm^2 are given in Fig. 2.

Discussion

The special feature of a methanol/air cell as described above is a high Ah-capacity per unit volume or per unit weight: 5.000 Ah/litre methanol, up to 1.000 Ah/l fuel-electrolyte mixture, or about 3 kg/kWh for an operating time 6.000 hours.

The experimental results reveal, however, the following disadvantages:

(i) The current densities at the fuel electrode at ambient temperatures are relatively low, if small amounts of noble metal catalysts are used.

(ii) The vapour pressure is unfavourable for moderate temperature applications.

(iii) With decreasing temperature the power output of the cell drops considerably.

FORMIC ACID AND FORMATE AS FUEL

Anodic oxidation of formic acid, nature of the intermediate product

In acid electrolytes methanol and formaldehyde are less reactive than formic acid (9,12,13). The oxidation rate at potentials $\varphi <$ 0.6 volt (vs. SHE) is determined by the poisoning effect of an intermediate product. The particles adsorbed at a Pt-electrode are probably formate radicals and certainly not carbon monoxide or oxalic acid (14). A potentiostatic potential scan is especially suited to give a qualitative view of the reaction mechanism. Fig. 3 shows three current peaks during the anodic scan. The first maximum is due to the reaction step (14)

$$HCOOH_{ad} \longrightarrow HCOO_{ad} + H^+ + e^- \quad \text{or}$$

$$HCOOH_{ad} \longrightarrow COOH_{ad} + H^+ + e^-$$

In the region of the second and third peaks the fuel reacts with chemisorbed oxygen as described above for the methanol oxidation. The adsorbed intermediate too is oxidized in this potential range. Fig. 4 clearly demonstrates the poisoning

effect of the adsorbed product on a smooth platinum electrode at 0.5 volt.

Application of a mixed Pt/Ru-catalyst

Recently Frumkin (15) has discovered that the use of a mixed platinum ruthenium catalyst diminishes the poisoning effect. This has been confirmed by the following experiment. An active carbon electrode (geom. surf. 24 cm^2, 12 mg Pt-metal/cm^2) was prepared (a) with 3 % Pt (b) with 3 % Pt/Ru (9:1) ratio by weight. The current densities observed at the two electrodes at 0.5 volt were for electrode (a) 2 mA/cm^2 and for electrode (b) 10 mA/cm^2. In a long duration experiment with an HCOOH/air cell (50cm^2 electrodes, 20°C) the ratio of power outputs using the two types of electrode was about 3. The current yield which is about the same for the two cells is surprisingly low, less than 20 % on a 2 electron/molecule basis.

Formate ion-oxidation on mixed noble metal catalysts

In early investigations of the anodic oxidation of methanol in alkaline solution with Raney-nickel (9) or platinum (6,10) electrodes formate ion was usually found as the primary oxidation product. The further oxidation of the formate ions occured at a less favourable potential. Grimes and Spengler (10), however, have observed that the use of mixed platinum and palladium catalysts allows the complete oxidation of methanol to carbonate. A formate ion/oxygen fuel cell with a nickel substrate as anode (9 mg Pd/Pt (5:1)/cm^2) produced twice the power output of a similar methanol cell at the same temperature.

These results demonstrate that the oxidation rate of formate ions is very sensitive to the composition and the structure of the metal catalyst. Moreover, the electrocatalytic effects are different for formate ion and methanol.

Our studies have shown that the formate oxidation rate on platinum and palladium alloys varies over more than two orders of magnitude. The formate oxidation has been investigated on a series of smooth metal electrodes by use of the potentiostatic scanning method. An example of the current voltage dia-

grams obtained in 6 N KOH + 4 M HCOOH is given in Fig. 5. The height of the high anodic current peak (during the anodic scan) is taken as measure of the catalytic activity of the metal. The activity of the metal surface is controlled by the potential range covered and the scanning speed (100 mV/sec). Fig. 6 shows the strong influence of the electrode material on the peak current density for 20 and 40°C.

The relationship between electrode material and current density obtained offers of course only a first insight into the selection of the most suitable catalyst. In battery practice one has to deal with porous electrodes and continuous discharge. Therefore factors other than metal composition are also important.

In preliminary tests of formate ion/air cells about 10 times the power output compared with methanol as fuel has been observed. Continuous discharge at 20 mA/cm^2 at 20°C is readily obtained.

Discussion

By use of mixed Pt/Ru-anode catalysts the power output of a HCOOH/air cell at ambient operating conditions is of the same order as that of an alkaline methanol/air cell. The reaction product of the formic acid cell is CO_2 and therefore electrolyte renewal is not required. On the other hand one needs for both electrodes noble metal catalysts. Another disadvantage is the high rate of the current-less decomposition. The influence of the current density on the reaction yield has not yet been investigated.

Due to the moderate current densities at ambient temperature and pressure the formate ion/air cell with mixed Pt-metal catalysts at the fuel electrode offers a new field of applications. In contrast to methanol the vapour pressure is low, so that operating temperatures up to 100°C can be used. Compared to methanol, however only 2 electrons per molecule are obtainable.

EXPERIMENTS WITH GLYCOL AS FUEL

In acid electrolytes the anodic oxidation of glycol leads to CO_2 as end product. The working potential is, however, less favourable than with formic acid as fuel (9). The oxidation at alkaline pH results in the formation of oxalate. But at moderate temperatures (60 - 90°C) a strong dehydrogenation takes place

$$CH_2OH\text{-}CH_2OH + 2\ OH^- \longrightarrow C_2O_4^{--} + 8\ H_{ad}$$
$$8\ H_{ad} + 8\ OH^- \longrightarrow 8\ H_2O + 8\ e^-$$

and current densities up to 600 mA/cm^2 can be obtained (9,16).

Grüneberg et al (9,16,17) have developed a glycol/air cell operating at ambient temperature and pressure.

The air electrode was pressed from activated carbon and polyethylene powder (500 kg/cm^2, 160°C) and built up in two layers. The layer on the electrolyte side was made only weakly hydrophobic and contained Ag_2O as catalyst. The electrode had such good mechanical stability that it could be used as an end plate in the cell. Between the air electrodes there is a fuel electrode of the same size: coarse grained Ni-DSK (3) is held in place by nickel screens.

The open circuit potential of such a cell (6 N KOH + 2 M glycol) is about 1.1 volt. At a load of 3 mA/cm^2 such a cell will have a potential of 0.8 volt at room temperature. For short periods of time current densities up to 30 mA/cm^2 can be withdrawn.

For the investigation of high current density glycol/air cells we have used as fuel electrodes, flame-sprayed Raney-nickel on a nickel substrate. Electrodes up to a geometric area of 20 x 30 cm^2 have been studied. As already stated by Boies and Dravnieks (18) the activity of the electrode is critically dependent on the grain size, and the substrate must be carefully prepared to obtain good and stable contact to the catalytic layer. The increase of the dehydrogenation rate with temperature has a strong influence on the shape of the current/voltage-curve (Fig. 7).

The featuresof the glycol cell operating at moderate temperatures are:

noble metal catalysts are not required, high current densities can be obtained in direct oxidation from an easily handled liquid fuel, and strong gas evolution does not take place. The price of the fuel and the necessary renewal of the electrolyte are the main disadvantages.

APPLICATIONS OF ALCOHOL AIR/CELLS

General Remarks

Ambient air cells with methanol or formate ion as fuel are particularly suited for a maintenance-free, continuous operation at low or moderate current densities. Therefore they could be used to supply signal devices, stationary or mobile communication systems, isolated weatherstations etc. Such alcohol/air cells can start to compete with dry batteries and wet batteries of the system zinc/NaOH/air.

The high power glycol cell should be applicable e.g. as an emergency unit. In contrast to such a fuel cell the presently used Diesel engine has several disadvantages:
it requires maintenance, unreliability of the rotating parts, uncertain starting in an emergency.

Beside battery construction cost, fuel cost and availability, the amount of noble metal used for the electrodes is a peculiar problem in commercial fuel cell application. In the alkaline methanol and formate cells developed so far 2 - 5 mg/cm^2 platinum and palladium are needed. To what extend this amount has to be decreased to make such cells economic depends very much on the special application.

Test of a 60 Watt methanol/air battery for sea buoys

On the basis of our laboratory investigations described above Brown, Boveri a. Cie. have built a 6 volt 10 amp battery for a flashing buoy. The module contains 10 cylindrical cells (Fig. 8). In each cell 18 pairs of electrodes are connected in parallel in order to equalize the different performance of the individual cells and to prevent the failure of single electrodes. From the 400 litre fuel/electrolyte-mixture 180 kWh

can be obtained. By using an electronic device the power output of the battery is stabilised (30 Watt in signal operation between 5 and 30°C) against changes of temperature and changes in fuel concentration which occur over a two years period of operation (intermittend 2 sec load, 4 sec O.C.).

The battery is presently in field test for serveral months. It is felt that the operation cost (methanol and caustic) will be cheaper than the present propane-consuming buoys.

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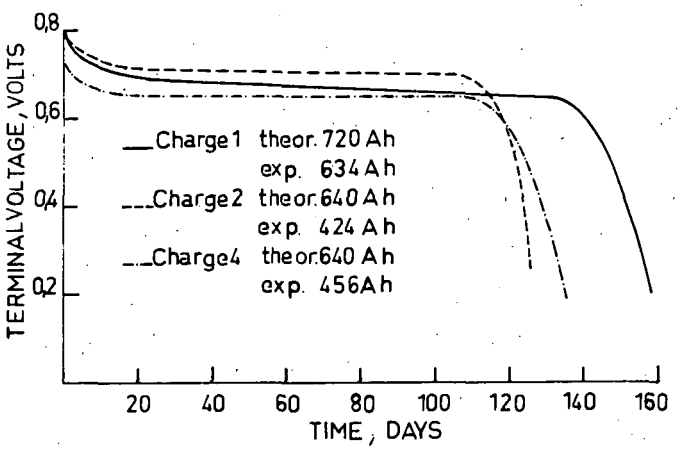

Fig. 1 Terminal voltage at periodic loads (2 sec load and 4 sec O.C.) of a methanol/air cell, operating time $\tau >$ 12.000 hours with 4 electrolyte charges, temperature 10 - 20°C

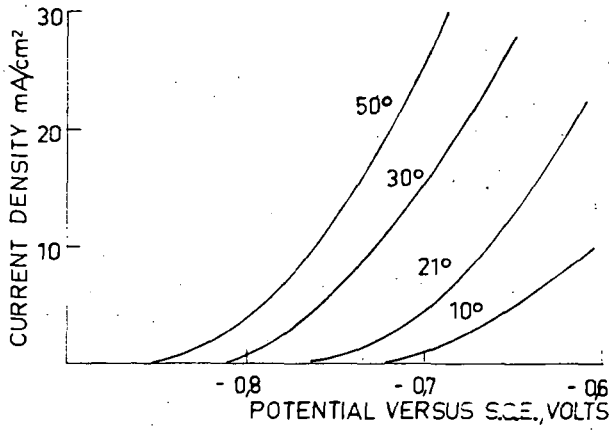

Fig. 2 Effect of temperature on the performance of a platinum activated carbon electrode in 6 N KOH + 2 M CH_3OH solution, F = 12 cm^2, 4.8 mg Pt/cm^2; curves taken after 1 day operation at 10 mA/cm^2

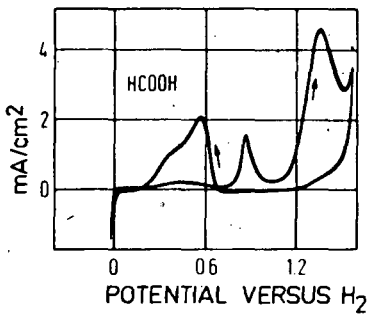

Fig. 3 Triangular potential scan on smooth Pt in 1 N H_2SO_4 + 1 M HCOOH, 50 mV/sec, 20°C

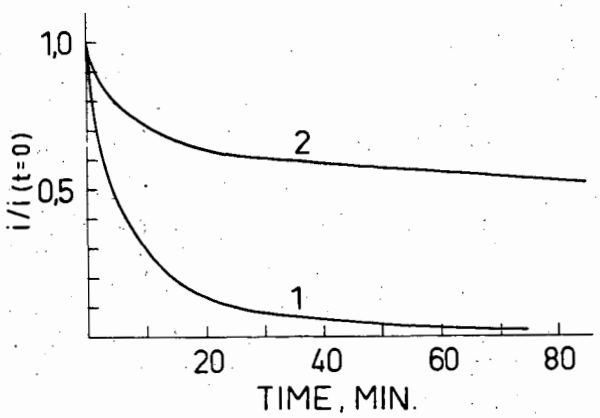

Fig. 4 Decrease of current with time on smooth Pt in 1 N H_2SO_4 + 1 M HCOOH at constant potential
(1) at 0.5 volt (first current peak in Fig. 3)
(2) at 0.9 volt (second peak in the anodic scan of Fig. 3)

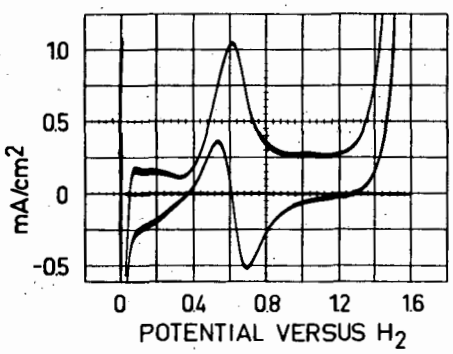

Fig. 5 Triangular potential scan on smooth Pt/Ir (75:25)-alloy in 6 N KOH + 4 M HCOOK, 100 mV/sec, 40°C

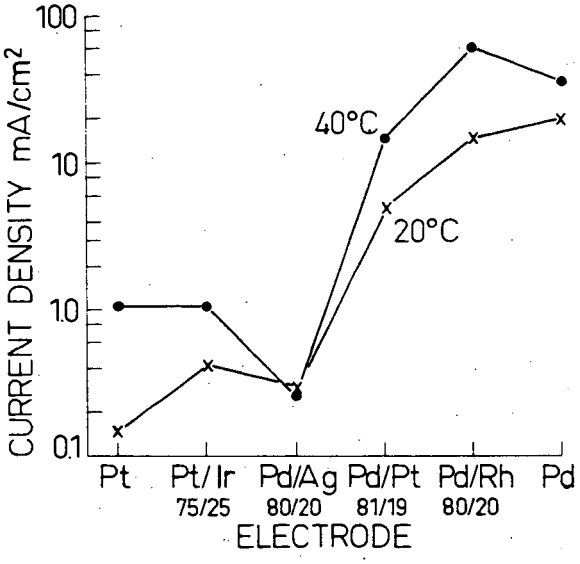

Fig. 6 Peak current density of a triangular potential scan according to Fig. 5 on different smooth metal electrodes in 6 N KOH + 4 M HCOOK

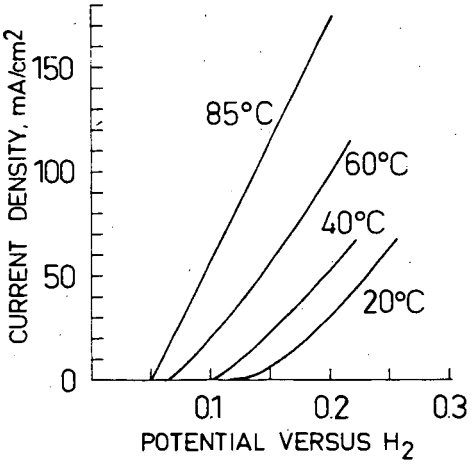

Fig. 7 Current density-potential curves on flame sprayed Raney-nickel (grain size 200 μ) in 6 N KOH + 2 M Glycol, plots taken after 2 day operation at 50 mA/cm^2

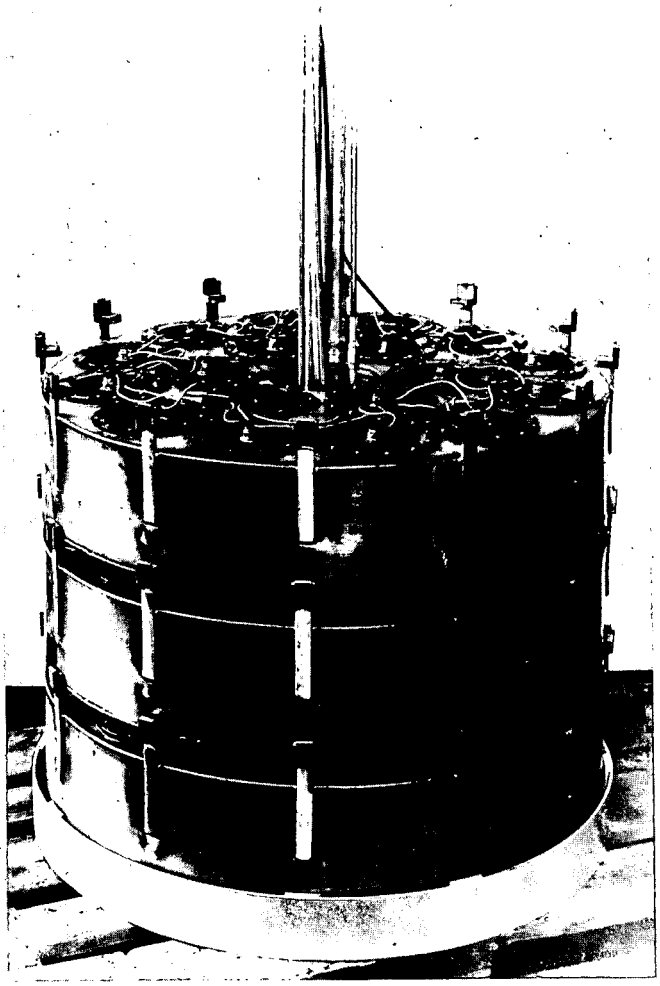

Fig. 8 Three cells of a 10 cell 60 Watt-methanol/air battery with cylindrical air diffusion electrodes for a flashing sea buoy
(by courtesy of Brown, Boveri and Cie., Baden/Schweiz)